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Spectroscopic Evidence of Uranium-Carboxyl Interaction at the Bacterial Cell Surface

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Beamline(s): X1A

Introduction: The interaction of microorganisms with radionuclides must be understood in order to adequately describe the behavior and fate of radioactive contaminants in the natural environment. Bacteria can biotransform uranium resulting in either insoluble species due to reductive precipitation or soluble species due to formation of carbonate complexes or biocolloids[1,2,3]. Here we focus on biosorption of U in order to gain a mechanistic understanding of the association of uranium with bacteria. The unique imaging and spectroscopy capability of soft x-ray spectromicroscopy is used to elucidate the chemical environment of C in the bacterial cell.

Methods and Materials: The anaerobic glucose fermenting bacterium *Clostridium* sp. has been shown to reduce U(VI) to U(IV) in growing culture[1]. For this study the culture was grown under optimal conditions and whole bacterial cells recovered. Cell wall fragments were prepared by passage through a French pressure cell (20,000 psi). After exposure to 0.08 mM uranyl nitrate at pH 5 the cells and walls were examined on the outboard branch of the X1A beamline over the 284-320 eV energy range for C-1s absorption fine structure.

Results: Whole cells of *Clostridium* sp. unexposed and exposed to U, imaged at 288 eV, are shown in Figure 1. Exposure to U resulted in the production of an exudate, rich in inorganic material (possibly P or U) at the margin of the cell. Carbon K-edge XANES of whole cells did not provide evidence of U interaction with specific C groups. However, analysis of cell wall fragments of *Clostridium* sp. showed a shift in the carboxylate absorption edge to a higher energy due to the presence of uranium (Figure 2). Carbonate was also formed in walls exposed to U (290 eV).

Conclusions: The carboxylate groups associated with cell surface species (sugars and amino acids) are expected to be ionized at pH 5 thus playing a major role in sorption of cations. This study shows the influence of UO_2^{2+}, an electron withdrawing cation, on the 1s-π^* resonance at the C-O absorption edge of *Clostridium* sp. cell walls. The influence of U on C K-edge XANES was not detected in whole cells. This was attributed to the overwhelming signal from an abundance of carboxyl moieties that did not participate in U uptake.

References: 1. Francis, A., Dodge, C., Lu, F., Halada, G., and Clayton, C., *Environ. Sci. Technol.* 28, 636 (1994). 2. Francis, A., Dodge, C., Gillow, J., and Papenguth, H., *Environ. Sci. Technol.* 34, 2311 (2000). 3. Gillow, J., Dunn, M., Francis, A., Lucero, D., and Papenguth, H. *Radiochim. Acta* 88, 769 (2000).

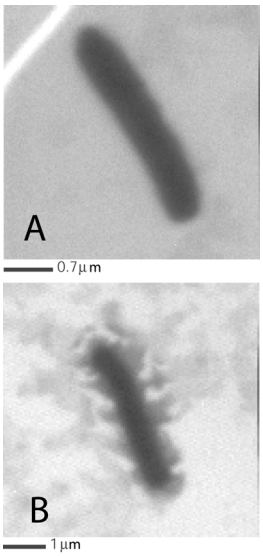

Figure 1. *Clostridium* sp. unexposed (A) and exposed to U (B).

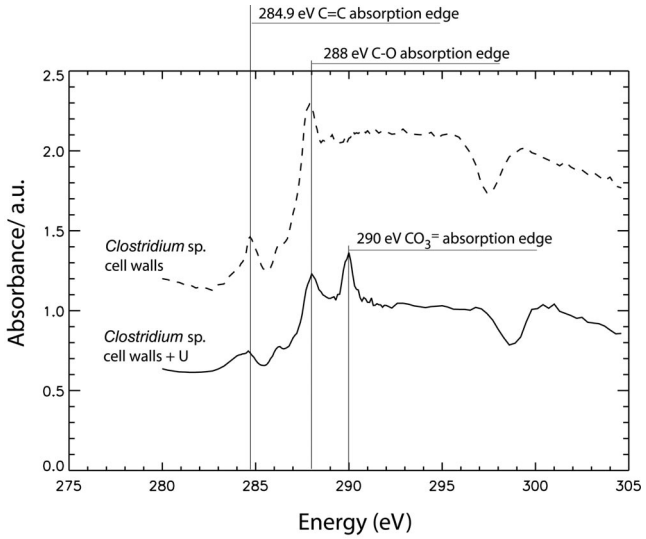

Figure 2. C-1s XANES of *Clostridium* sp. cell walls; the carboxyl absorption feature (288 eV) is shifted to higher energy in the presence of uranium.